

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Alkylation of Hydroxy Aromatic Compounds

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organised under the Laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a process for the alkylation of aromatic compounds containing at least one hydroxy substituent. This invention is particularly concerned with an improved process for the alkylation of a phenol in which a high yield of the para isomer of the alkylated phenol is obtained.

The alkylation of phenols with alcohols, alkyl halides, and olefins is old per se. It is well known that the benzene nucleus in phenolic compounds is very susceptible to alkylation in the presence of conventional alkylation catalysts. However, this very ease of alkylation often is a disadvantage when the synthesis of specific mono-alkyl derivatives of phenols is desired. Difficulties encountered in processes for the production of such specific mono-alkyl derivatives may be attributed to the reactivity of the phenolic group toward alkylating agents, giving rise to undesirable aralkyl ethers. Prior art processes teach that alkylphenols can be conventionally produced by a batch procedure but substantially complete conversion of phenol must be obtained since free phenol in the product leads to sludge formation and other undesirable effects in subsequent operations. The batch procedure also has a number of other inherent disadvantages. For example, when olefin is added to a phenol-boron fluoride mixture, no reaction occurs until a brief induction period has elapsed, after which the highly exothermic

reaction is initiated with almost explosive violence. The quality of the final product is therefore frequently impaired since reaction temperatures are quite difficult to control at this point. As a result, considerable time is often required to effect complete addition of the olefin in order to prevent reaction temperature "run-aways" and reduce the content of unreacted phenol to a low level. In addition, products from different batches sometimes vary over a wide range of compositions. These inconsistencies in composition lead to subsequent processing difficulties and to lowering of product quality of derivatives of the alkylated phenols.

In continuous processes of the prior art, high temperatures and/or high pressures are utilized with conventional catalysts. These continuous processes for the production of substantially pure alkylphenols of high molecular weight have been time consuming and expensive, and have usually resulted in low concentrations of the desired isomer.

The present invention relates to a process for the alkylation of an aromatic compound containing at least one hydroxy substituent wherein said aromatic compound is reacted with an olefin in the presence of an acid-acting refractory inorganic oxide catalyst and a reaction product containing at least two isomeric forms of an aromatic compound having at least an alkyl substituent and a hydroxy substituent is recovered, and the present invention is characterized in that the proportion of the isomeric form having the alkyl substituent in a position para to the hydroxy-substituent, relative to the total alkylated product, is increased by effecting the reaction in the presence of more than 0.08 weight per cent but less than 5 weight percent of water based on the total feed to the alkylation zone production of high yields of the para isomer of alkylated

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hydroxy aromatic compounds in a continuous operation is preferably accomplished by effecting the reaction of the olefin with the hydroxy aromatic compound in the presence of at least about 0.5 weight percent of water. 70

According to a specific embodiment of the invention, phenol is alkylated with propylene trimer in the presence of silica-alumina and a small amount of water at a temperature in the range of 25° to about 250°C. and at a pressure in the range of atmospheric to about 100 atmospheres. Paranonylphenol is produced in excellent yield. The total nonylphenol product analyzed as 97 weight percent para-nonylphenol, 1 weight percent meta-nonylphenol and 2 weight percent ortho-nonylphenol. The presence of a small amount of water during the alkylation produced a greater ncnene conversion and a more selective reaction since the concentration of the desired para isomer increased toward the equilibrium composition. 75

Suitable aromatic compounds containing at least one hydroxy substituent which may be used in the present process include both mono- and polyhydric phenols such as phenol, resorcinol, catechol, o-cresol, m-cresol, o-ethylphenol, m-ethylphenol, the corresponding isomeric propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl and undecyl-phenols; alkyl and cycloalkyl ethers of the polyhydric phenols which contain at least one free hydroxy group, such as the ortho and meta isomers of methoxy-, ethoxy-, propoxy- and butyloxyphenol; also the 2,6- and 2,3-isomers of dimethoxy- and diethoxyphenol, ortho- and metacyclopentoxy-, cyclohexoxy- and cycloheptoxyphenol. Other nuclear-substituted derivatives of phenol can be used, such as the ortho- and meta-substituted halo- and nitro-phenols. It is also contemplated within the scope of this invention to alkylate polynuclear aromatic compounds containing at least one hydroxy substituent. 80

Suitable alkylating agents comprise monolefins and poly-olefins. Olefins which are employed in the present process may be either normally gaseous or normally liquid and include ethylene, propylene, 1-butene, 2-butene and isobutylene; higher molecular weight olefins such as the various pentenes, hexenes and heptenes and mixtures thereof; various polymers of normally gaseous olefins such as propylene trimer, propylene tetramer and propylene pentamer; cyclic olefins such as cyclopentene, methylcyclopentene, cyclohexene and methylcyclohexene; conjugated diolefins such as butadiene and isoprene; non-conjugated diolefins and other polyolefins. The various olefinic hydrocarbons are not necessarily equivalent in their action as alkylating agents. Olefinic hydrocarbons present in products of thermal and catalytic cracking of oil, products from dehydrogenation of paraffinic hydrocarbons or products resulting from dehydra- 85

tion of alcohols may also be utilized as alkylating agents. 90

Catalysts which may be used to effect the alkylation of the aromatic compound containing at least one hydroxy substituent with the olefinic hydrocarbon comprise acid-acting refractory inorganic oxide catalysts such as silica-alumina, alumina treated with hydrogen fluoride, alumina treated with hydrogen chloride and alumina treated with boron fluoride. Other refractory inorganic oxides which also may be utilized as catalyst, although not necessarily with equivalent results, include titanium dioxide, zirconium dioxide, chromia, zinc oxide, silica-magnesia, silica-alumina-magnesia, silica - alumina - zirconia, chromia-alumina, alumino-boria and silica-zirconia. These refractory inorganic oxides may be treated with an acid. If acid treatment is desired, it is necessary that the inorganic oxide utilized must form a relatively stable compound with the acid so that the acid is not readily driven off by heat or reduced pressure. 95

The alkylation is carried out at temperatures in the range of from 25° to 250°C. or preferably from 50° to 150°C., and at pressures ranging from atmospheric to 100 atmospheres or more in the presence of a small amount of water. When the reaction is effected at temperatures in the lower portion of the indicated temperature range, atmospheric pressure will usually be employed. However, if the reaction is effected at temperatures in the higher portion of the range, superatmospheric pressures ranging from 2 to 100 atmospheres or more will be employed, the pressure being sufficient to maintain a portion of the reactants in the liquid phase. 100

The process of this invention may be effected in any suitable manner and may comprise a batch or a continuous type operation. The preferred method is a continuous type operation. In one particular method of continuous type operation, the aromatic compound containing at least one hydroxy substituent and the olefin are continuously charged to a reaction zone containing a fixed bed of the desired catalyst and maintained at the proper operating conditions of temperature and pressure. The reaction zone may comprise an unpacked vessel or coil or may be lined with an adsorbent packing material. The two reactants may be charged through separate lines or may be admixed prior to entry into the reaction zone. In order to maintain the presence of a small amount of water in the alkylation zone, the reactants may be used as received if their water level is sufficiently high, or the desired quantity of water may be charged through a separate line or may be admixed with the reactants prior to entry into said alkylation zone. Less than 5 weight percent but more than 0.08 weight percent of water, based on total feed charged, is main- 105

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tailed in the alkylation zone to promote the alkylation of the hydroxy-aromatic compound at the desired para position. Upon completion of the residence time, the reaction mixture is 5 continuously withdrawn and the desired products are separated therefrom by conventional means. Unconverted reactants may be recharged to the reaction zone as a portion of the starting material. Another continuous type 10 operation comprises the moving bed type in which the reactants and the catalyst bed move either concurrently or countercurrently to each other while passing through the reaction zone. Yet another continuous type of operation which 15 may be used is the slurry type in which the catalyst is carried into the reaction zone as a slurry in one of the reactants. Still another type of operation which may be used is the 20 batch type operation in which a quantity of the aromatic compound containing at least one hydroxy substituent, the olefin and the catalyst are placed in an appropriate apparatus such as, for example, a rotating or stirred autoclave or an alkylation flask. The apparatus 25 is then heated to and maintained at the desired temperature for a predetermined residence time at the end of which time the reaction mixture is cooled to room temperature. The desired reaction product is recovered by 30 conventional means such as, for example, by washing, drying, fractional distillation or crystallization.

The following examples are given to illustrate the process of the present invention.

35 **EXAMPLE I**
This example illustrates the effect of water in a process for the alkylation of aromatic compounds containing at least one hydroxy substituent when utilizing an acid-acting refractory inorganic oxide alkylation catalyst, namely silica-alumina. The processing unit 40 consisted of liquid and gas charge pumps, reactor, pressure controllers, fractionating columns, and liquid and gas collection 45 systems.

Phenol and nonene were pumped separately into the reactor which was maintained at an outlet pressure of 17.7 atmospheres and at 185°C., with a water concentration of 0.1 50 weight percent. At a residence time of 0.5 hours, and with a phenol-nonene mol ratio of 3.2, 92 weight percent of the nonenes were converted, and 87 weight percent of the phenol which reacted was converted to para-nonylphenol, 10 weight percent to the ortho-nonylphenol and 3 weight percent to the meta-nonylphenol.

In a second experiment, phenol, nonene and 55 a silica-alumina catalyst were again used, and the reactor was maintained at essentially the same conditions as above but with a water level of about 0.5 weight percent. The presence of this amount of water in the alkylation zone proved beneficial since high conversion of the 60

phenol to the desired para-nonylphenol isomer was again obtained. The nonylphenol product recovered contained 97 weight percent para-nonylphenol, 2 weight percent ortho-nonylphenol and 1 weight percent meta-nonylphenol. 65

The quantities of the principal components of the fractions of distillates were determined by mass spectrometer analyses, and the isomeric distribution of the nonylphenol was based on infrared data.

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EXAMPLE II 75
This example illustrates the process of the present invention utilizing alumina treated with boron trifluoride as the acid-acting refractory inorganic oxide catalyst. The reaction conditions employed were the same as in Example I.

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o-Cresol and isobutylene were pumped separately to the reactor which was maintained at 34 atmospheres and about 250°C. with a water level of about 0.2 weight percent. The presence of this amount of water proved beneficial since high conversion to the desired para-butylcresol isomer was again obtained.

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EXAMPLE III 90
This example illustrates the process of the present invention utilizing alumina-boria as the acid-acting refractory inorganic oxide alkylation catalyst.

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o-Cresol and propylene trimer (nonene) were pumped separately to the reactor maintained at 20.4 atmospheres and about 150°C. with a water level of about 0.75 weight percent. A good yield of the desired para-nonylcresol isomer was obtained.

100 **WHAT WE CLAIM IS:—**

1. Process for the alkylation of an aromatic compound containing at least one hydroxy substituent wherein said aromatic compound is reacted with an olefin in the presence of an acid-acting refractory inorganic oxide catalyst and a reaction product containing at least two isomeric forms of an aromatic compound having at least an alkyl substituent and a hydroxy substituent is recovered, characterized in that the proportion of the isomeric form having the alkyl substituent in a position para to the hydroxy substituent, relative to the total alkylated product, is increased by effecting the reaction in the presence of more than 0.08 weight percent but less than 5 weight percent of water based on the total feed to the alkylation zone.

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2. Process according to claim 1 characterized thereby that the reaction is effected in the presence of at least about 0.5 weight percent but less than 5 weight percent of water based on the total feed to the alkylation zone.

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3. Process according to claim 1 or 2 characterized thereby that the acid-acting refractory inorganic oxide is silica-alumina.

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4. Process according to claim 1 or 2 characterized thereby that the acid-acting refractory

inorganic oxide is alumina treated with hydrogen fluoride.

5. Process according to claim 1 or 2 characterized that the acid-acting refractory inorganic oxide is alumina treated with boron trifluoride.

6. Process according to any of the claims 1 to 5 characterized in that the alkylation is effected at a temperature of from 25° to 250°C. and at a pressure of from atmospheric 10 to 100 atmospheres.

7. Process according to any of the claims 1 to 6 characterized in that the aromatic com-

pound having the hydroxy substituent is phenol, the olefin is propylene trimer and para-nonylphenol is recovered.

8. Process for the alkylation of an aromatic compound containing at least one hydroxy substituent substantially as described.

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